

Heterogeneous & Homogeneous & Bio- & Nano-

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CATALYSIS

Supporting Information

Photocatalyst-free, Visible Light Driven, Gold Promoted Suzuki Synthesis of (Hetero)biaryls

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Table of contents:

General Methods	S2
Optimization of the catalytic system	S3
Characterization of biaryls 3	S7
^1H NMR spectra of compounds 3	S10

General Methods

¹H and ¹³C NMR spectra were recorded on a 200 MHz or a 400 MHz spectrometer. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard (deuterochloroform: 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sext = sextet, sept = septet, p = pseudo, b = broad, m = multiplet), coupling constants (Hz). GC-MS spectra were taken by EI ionization at 70 eV on a Hewlett-Packard 5971 with GC injection. They are reported as: *m/z* (rel. intense). Chromatographic purification was done with 240-400 mesh silica gel. Melting points were measured using open glass capillaries in a Bibby Stuart Scientific Melting Point Apparatus SMP 3 and are calibrated by comparison with literature values (Aldrich). Compounds **1a-g** and **1'a** have been prepared by following a known procedure.^[1] Boronic acids **2a-g** as well as the catalyst PPh₃AuCl and the employed additives were commercially available and used as received.

General procedure for the gold catalysed synthesis of (hetero)biaryls **3.** All the following reactions were set up in a 3mL Pyrex vial. To a solution (200 µL, CH₃CN:CH₃OH = 3:1, reagent grade) of aryl azosulfone **1** (0.1 mmol, 0.5 M) was added the boronic acid **2** (0.2 mmol, 2 equiv.), NaOAc (0.2 mmol), PPh₃AuCl (5 mol%) and bpy (20 mol%) in sequence. The resulting mixture was then degased via N₂-bubbling and the vial irradiated with a 7W or a 1W blue LED while stirring until the complete consumption of the starting substrate **1** (checked by TLC monitoring) the solvent was removed under vacuum and reaction crude purified via flash chromatography.

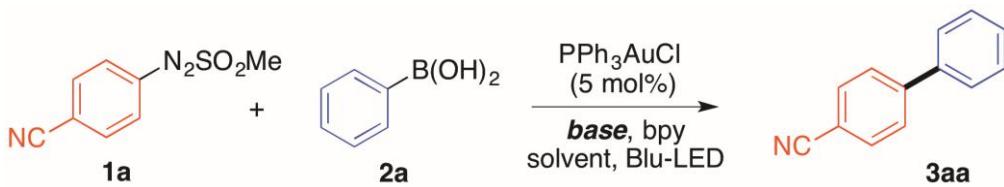
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Optimization of the catalytic system:

Table S1: The base

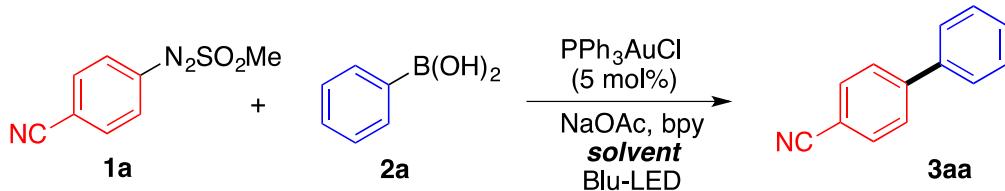
Entry	base	3aa (% Yield) ^[a]
1	NaOAc	51
2	KOAc	41
3	CsOAc	43
4	Na ₂ CO ₃	46
5	tBuCO ₂ Na	39
6	NaHCO ₃	35
7	Na ₂ HPO ₄	35
8	Li ₂ CO ₃	28
9	CsF	20
10	K ₂ CO ₃	18
11	Cs ₂ CO ₃	11
12	tBuONa	0
13	--	0
14 ^[b]	TEA	22

Conditions: **1a:2a:base:bpy=1:2:2:0.2,rt, 7 W-blue LED, 600μL MeCN, overnight.** ^[a] Isolated yields. ^[b] 200 μL MeCN.

Table S2: The concentration

Entry	Base	Conc. (mol/L)	3aa (% Yield) ^[a]
1	Na ₂ CO ₃	0.50	58
2	Na ₂ CO ₃	1.00	48
3	Na ₂ CO ₃	0.17	46
4	Na ₂ CO ₃	0.05	28
5	NaOAc	0.50	56
6	NaOAc	0.17	51
7	NaOAc	0.10	45
8	tBuCO ₂ Na	0.50	48
9	tBuCO ₂ Na	0.17	39

Conditions: **1a**:**2a**:base:bpy = 1:2:2:0.2, rt, 7 W blue-LED, MeCN, overnight. ^[a] Isolated yields.

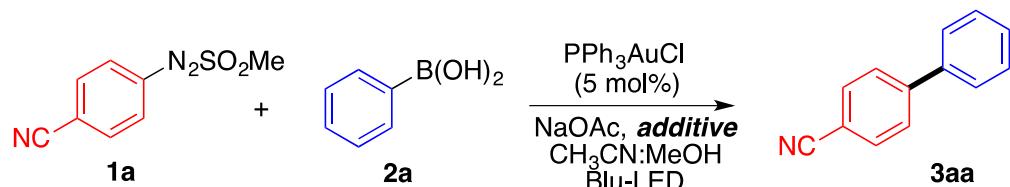
Table S3: The solvent

Entry	Additive	3aa (% Yield) ^[a]
1	CH ₃ CN/MeOH (3:1)	61
2	CH ₃ CN	56
3	CH ₃ CN/H ₂ O (20:1)	57
4	CH ₃ CN/H ₂ O (3:1)	28
5	CH ₃ CN/tBuOH (3:1)	39
6	THF	36
7	DMF	17

Conditions: **1a**:**2a**:NaOAc:bpy = 1:2:2:0.2, rt, 7 W blue-LED, solvent, overnight.

^[a] Isolated yields.

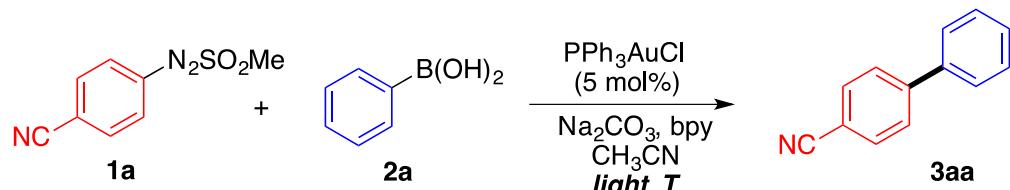
Table S4: The additive



Entry	additive	Loading (mol%)	3aa (% Yield) ^[a]
1	bipyridine	20	61
2	6,6'-Br ₂ -bipyridine	20	53
3	4,4'-MeO ₂ -bipyridine	20	50
4	4,4'-Ph ₂ -bipyridine	20	45
5	di-2-pyridyl-methanone	20	41
6	6,6'-Ph ₂ -bipyridine	20	36
7	1,10-phenanthroline	20	46
8	4,4'-tBu ₂ -bipyridine	20	36
9	4,4'-Br ₂ -bipyridine	20	28
10	5,5'-Me ₂ -bipyridine	20	17
11 ^[b]	none	--	17
12	TEMPO	120	10

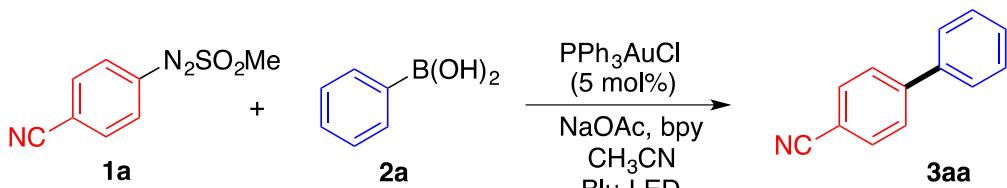
Conditions: **1a**:**2a**:base:bpy = 1:2:2:0.2, rt, 7 W blue-LED, MeCN:MeOH = 3:1, overnight. ^[a] Isolated yields. ^[b] Reaction carried out with Tos derivative **1a'**.

Table S5: Light and temperature roles



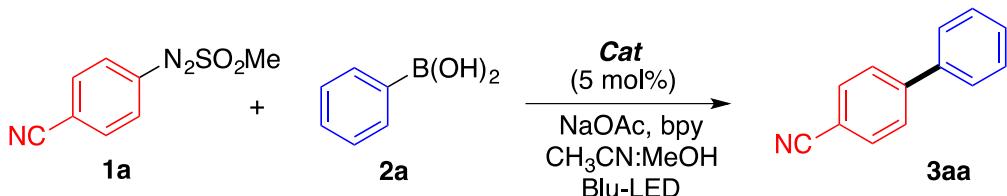
Entry	Light	T (°C)	3aa (% Yield) ^[a]
1	7 W Blue-LED	25	46
2	7 W Blue -LED	36	40
3	24 W Blue -LED	43	36
4	7 W Blue -LED	15	35
5	7 W Blue -LED	-7	26
6	7 W White-LED	25	46
7	none	25	15

Conditions: **1a**:**2a**:base:bpy = 1:2:2:0.2, 600 μL CH₃CN, overnight. ^[a] Isolated yields.

Table S6: 1a:2a ratio

Entry	1a:2a	3aa (% Yield) ^[a]
1	1:2	36
2	2:1	46
3	4:1	32

Conditions: **1a:2a:base:bpy** = x:y:2:0.2, 600 μL CH₃CN, irradiated overnight. ^[a] Isolated yields.

Table S7: The gold complex

Entry	Cat(mol%)	3aa (% Yield) ^[a]
1	PPh ₃ AuCl (5)	61 (65) ^[b]
2	PPh ₃ AuCl (20)	53
3	PPh ₃ AuNTf ₂ (5)	57
4	IPrAuNTf ₂ (5)	50
5	-	< 1

Conditions: **1a:2a:base:bpy** = 1:2:2:0.2, CH₃CN:MeOH (3:1, 0.5 M in **1a**), irradiated overnight. ^[a] Isolated yields. ^[b] Between brackets NMR-yield.

Characterization of bi-aryls 3

	3aa. ^[2] Yield: 61% (reaction time = 16 h, 7 W Blue LED). Colourless solid. <i>c</i> Hex/EtOAc = 95:5, MP: 87-89 °C (lit. MP: 87 °C), GC-MS: 179 m/z, 1H-NMR (400 Hz, CDCl ₃): δ = 7.41-7.45 (m, 1H), 7.48-7.50 (m, 2H), 7.60-7.62 (m, 2H), 7.68-7.75 (m, 4H) ppm. 13C-NMR (100 Hz, CDCl ₃): δ = 110.9, 118.9, 127.2(2C), 127.7(2C), 128.6, 129.1(2C), 132.6(2C), 139.1, 145.6 ppm. 4,4'-dicyanobiphenyl (3a') was also isolated in 20% yield as the byproduct. 3a' ^[3] GC-MS: 204 m/z. 1H-NMR (400 Hz, CDCl ₃): δ = 7.69 (d, <i>J</i> = 8.0 Hz, 4H), 7.78 (d, <i>J</i> = 8.0 Hz, 4H) ppm.
	3ab. ^[4] Yield: 45% (reaction time = 16 h, 7 W Blue LED). Colourless solid. <i>c</i> Hex/EtOAc = 95:5, MP: 107-108 °C (lit. MP: 109-110 °C), GC-MS: 193 m/z, 1H-NMR (400 Hz, CDCl ₃): δ = 2.43 (s, 3H), 7.29 (d, <i>J</i> = 7.6 Hz, 2H), 7.50 (d, <i>J</i> = 8.0 Hz, 2H), 7.65-7.71 (m, 4H) ppm.
	3ac. ^[2] Yield: 45% (reaction time = 16 h, 7 W Blue LED). Colourless solid. <i>c</i> Hex/EtOAc = 95:5; MP: 102-105 °C (lit. MP: 104 °C), GC-MS: 179 m/z, 1H-NMR (400 Hz, CDCl ₃): δ = 3.88 (s, 3H), 7.01 (d, <i>J</i> = 8.8 Hz, 2H), 7.57 (d, <i>J</i> = 8.8 Hz, 2H), 7.64 (d, <i>J</i> = 8.0 Hz, 2H), 7.70 (d, <i>J</i> = 8.0 Hz, 2H) ppm.
	3ad. ^[5] Yield: 55% (reaction time = 16 h, 7 W Blue LED). Colourless solid. <i>c</i> Hex/EtOAc = 95:5; MP: 188-191 °C (lit. MP: 188-190 °C), GC-MS: 255 m/z, 1H-NMR (400 Hz, CDCl ₃): δ = 7.38 (t, <i>J</i> = 8.0 Hz, 1H), 7.46 (t, <i>J</i> = 7.6 Hz, 2H), 7.62-7.73 (m, 10H), ppm.
	3ae. ^[6] Yield: 37% (reaction time = 16 h, 7 W Blue LED). Colourless solid. <i>c</i> Hex/EtOAc = 95:5; MP: 115-117 °C (lit. MP: 116-118), GC-MS: 197 m/z; 1H-NMR (400 Hz, CDCl ₃): 7.17 (t, <i>J</i> = 8.7 Hz, 1H), 7.59-7.54 (m, 1H), 7.66-7.62 (m, 1H), 7.76-7.69 (m, 1H). 19F-NMR (377 Hz, CDCl ₃): δ = -113.2 (m, 1F) ppm.
	3af. ^[7] Yield: 40% (reaction time = 16 h, 7 W Blue LED). Pale red oil. <i>c</i> Hex/EtOAc = 95:5; GC-MS: 235 m/z; 1H-NMR (400 Hz, CDCl ₃): δ = 7.41-7.46 (m, 2H), 7.49 (s, 1H), 7.69-7.72 (m, 2H), 7.75-7.80 (m, 2H), 7.84-7.88 (m, 1H), 7.92-7.96 (m, 1H) ppm.
	3ba. ^[8] Yield: 45% (reaction time = 16 h, 1 W Blue LED). Colourless solid. <i>c</i> Hex/EtOAc = 95:5; MP: 110-111 °C (lit. MP: 109-110 °C), GC-MS: 196 m/z; 1H-NMR (400 Hz, CDCl ₃): δ = 2.66 (s, 3H), 7.41 (d, <i>J</i> = 7.2 Hz, 1H), 7.47-7.50 (m, 2H), 7.63-7.66 (m, 2H), 7.69-7.71 (m, 2H), 8.00-8.06 (m, 2H) ppm.

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	3bb. ^[9] Yield: 31% (reaction time = 40 h, 1 W Blue LED). White solid. <i>c</i> Hex/EtOAc = 93:7; MP: 116-117 °C (lit. MP: 116-118 °C); GC-MS: 210 m/z; 1H-NMR (400 Hz, CDCl ₃): δ = 2.39 (s, 3H), 2.63 (s, 3H), 7.24 (d, <i>J</i> = 7.8 Hz, 2H), 7.51 (d, <i>J</i> = 8.0 Hz, 2H), 7.65 (d, <i>J</i> = 7.8 Hz, 2H), 8.00 (d, <i>J</i> = 8.0 Hz, 2H) ppm.
	3bc. ^[6] Yield: 31% (reaction time = 16 h, 1 W Blue LED). White solid. <i>c</i> Hex/EtOAc = 9:1; MP: 155-157 °C (lit. MP: 156-157 °C); GC-MS: 226 m/z; 1H-NMR (400 Hz, CDCl ₃): δ = 2.64 (s, 3H), 3.88 (s, 3H), 7.00 (dd, <i>J</i> = 2.0, 6.8 Hz, 2H), 7.58 (dd, <i>J</i> = 2.0, 6.8 Hz, 2H), 7.65 (dd, <i>J</i> = 2.0, 8.0 Hz, 2H), 8.01 (dd, <i>J</i> = 2.0, 8.0 Hz, 2H) ppm.
	3bd. ^[10] Yield: 35% (by ¹ H-NMR, as a mixture with <i>p</i> -quarter phenyl, reaction time = 16 h, 7 W Blue LED). White solid, MP: 234-237 °C (lit. MP: 237-238 °C), <i>c</i> Hex/EtOAc = 95:5; GC-MS: 272 m/z; 1H-NMR (400 Hz, CDCl ₃): δ = 2.66 (s, 3H), 7.39 (d, <i>J</i> = 7.4 Hz, 1H), 7.48 (t, <i>J</i> = 7.4 Hz, 2H), 7.65-7.68 (m, 2H), 7.71-7.73 (m, 4H), 7.73-7.76 (m, 2H), 8.06 (d, <i>J</i> = 8.4 Hz, 2H) ppm.
	3bf. ^[11] Yield: 48% (reaction time = 16 h, 7 W Blue LED). Red solid. <i>c</i> Hex/EtOAc = 9:1; MP: 76-78 °C (lit. MP: 77-78°C); GC-MS: 252 m/z; 1H-NMR (400 Hz, CDCl ₃): δ = 2.68 (s, 3 H), 7.42-7.44 (m, 2H), 7.51 (s, 1H), 7.71 (d, <i>J</i> = 8.0 Hz, 2H), 7.91-7.96 (m, 2H), 8.06 (d, 2H, <i>J</i> = 8.4 Hz) ppm.
	3ca. ^[9] Yield: 40% (reaction time = 16 h, 1 W Blue LED). White solid, MP: 77-79 °C (lit. MP: 77-78°C). <i>c</i> Hex/EtOAc = 98:2; GC-MS: 184 m/z; 1H-NMR (400 Hz, CDCl ₃): δ = 3.87 (s, 3H), 7.00 (d, <i>J</i> = 8.8 Hz, 2H), 7.32 (d, <i>J</i> = 7.4 Hz, 1H), 7.43 (t, <i>J</i> = 8.0 Hz, 2H), 7.53-7.58 (m, 4H) ppm.
	3cb. ^[4] Yield: 28% (reaction time = 16 h, 1 W Blue LED). Light yellow solid. <i>c</i> Hex/DCM = 97:3; MP: 107-109 °C (lit. MP: 107-108°C); GC-MS: 198 m/z; 1H-NMR (400 Hz, CDCl ₃): δ = 2.39 (s, 3H), 3.86 (s, 3H), 6.97 (d, <i>J</i> = 8.8 Hz, 2H), 7.23 (d, <i>J</i> = 7.8 Hz, 2H), 7.45 (d, <i>J</i> = 7.8 Hz, 2 H), 7.51 (d, <i>J</i> = 8.8 Hz, 2H) ppm.
	3cd. ^[12] Yield: 38% (reaction time = 16 h, 1 W Blue LED). White solid. <i>c</i> Hex/DCM = 9:1; MP: 222-224 °C (lit. MP: 221-224°C); GC-MS: 260 m/z; 1H-NMR (400 Hz, CDCl ₃): δ = 3.88 (s, 3H), 7.01 (d, <i>J</i> = 9.2 Hz, 2H), 7.36 (t, <i>J</i> = 7.4 Hz, 1H), 7.47 (t, <i>J</i> = 7.6 Hz, 2H), 7.59 (d, <i>J</i> = 9.2 Hz, 2H), 7.63-7.75 (m, 6H) ppm.
	3ce. ^[13] Yield: 55% (reaction time = 16 h, 1 W Blue LED). Pale yellow solid. <i>c</i> Hex/EtOAc = 30:1; MP: 91-22 °C (lit. MP: 90-91°C); GC-MS: 202 m/z; 1H-NMR (400 Hz, CDCl ₃): δ = 3.86 (s, 3H), 6.98 (d, <i>J</i> = 8.8 Hz, 2H), 7.11 (d, <i>J</i> = 8.4 Hz, 2H), 7.47-7.52 (m, 2H) ppm. ¹⁹F-NMR (377 Hz, CDCl ₃): δ = -116.9 (m, 1F) ppm.
	3cf. ^[11] Yield: 44% (reaction time = 16 h, 1 W Blue LED). Colorless oil. <i>c</i> Hex/EtOAc = 9:1; GC-MS: 240 m/z; 1H-NMR (400 Hz, CDCl ₃): δ = 3.89 (s, 3H), 7.03 (d, <i>J</i> = 6.4 Hz, 2H), 7.34 (s, 1H), 7.38-7.41 (m, 2H), 7.51 (d, <i>J</i> = 6.4 Hz, 2H), 7.89-7.94 (m, 2H)

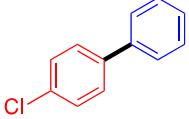
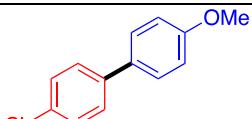
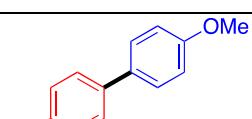
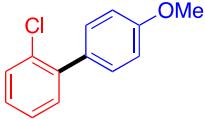
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	ppm.
	3da. ^[14] Yield: 40% (reaction time = 16 h, 1 W Blue LED). Orange solid. <i>c</i> Hex/DCM = 96:4; MP: 78-80 °C (lit. MP: 78-79 °C); GC-MS: 208 m/z; ¹H-NMR (400 Hz, CDCl ₃): δ = 3.85 (s, 3H), 6.96-6.99 (m, 2H), 7.36-7.39 (m, 2H), 7.46-7.51 (m, 4H) ppm.
	3dc. ^[15] Yield: 44% (reaction time = 16 h, 1 W Blue LED). Orange solid. <i>c</i> Hex/EtOAc = 80:3; MP: 108-110 °C (lit. MP: 111.1-111.3 °C); GC-MS: 218 m/z; ¹H-NMR (400 Hz, CDCl ₃): δ = 3.62 (s, 3H), 6.98 (d, <i>J</i> = 9.2 Hz, 2H), 7.38 (d, <i>J</i> = 9.2 Hz, 2H), 7.47-7.51 (m, 4H) ppm.
	3ec. ^[16] Yield: 39% (reaction time = 19 h, 1 W Blue LED). White solid. <i>c</i> Hex/EtOAc = 95:5; MP: 137-138 °C (lit. MP: 136-138 °C); GC-MS: 262 m/z; ¹H-NMR (400 Hz, CDCl ₃): δ = 3.86 (s, 3H), 6.98 (d, <i>J</i> = 8.8 Hz, 2H), 7.42 (d, <i>J</i> = 8.8 Hz, 2H), 7.49 (d, <i>J</i> = 8.8 Hz, 2H), 7.54 (d, <i>J</i> = 8.6 Hz, 2H) ppm.
	3fc. ^[17] Yield: 28% (reaction time = 16 h, 1 W Blue LED). Red oil. <i>n</i> Hex/Et ₂ O = 100:1; GC-MS: 218 m/z; ¹H-NMR (400 Hz, CDCl ₃): δ = 3.87 (s, 3H), 6.98 (d, <i>J</i> = 9.2 Hz, 2H), 7.28-7.36 (m, 3H), 7.40 (d, <i>J</i> = 9.2 Hz, 2H), 7.46-7.48 (m, 1H) ppm.

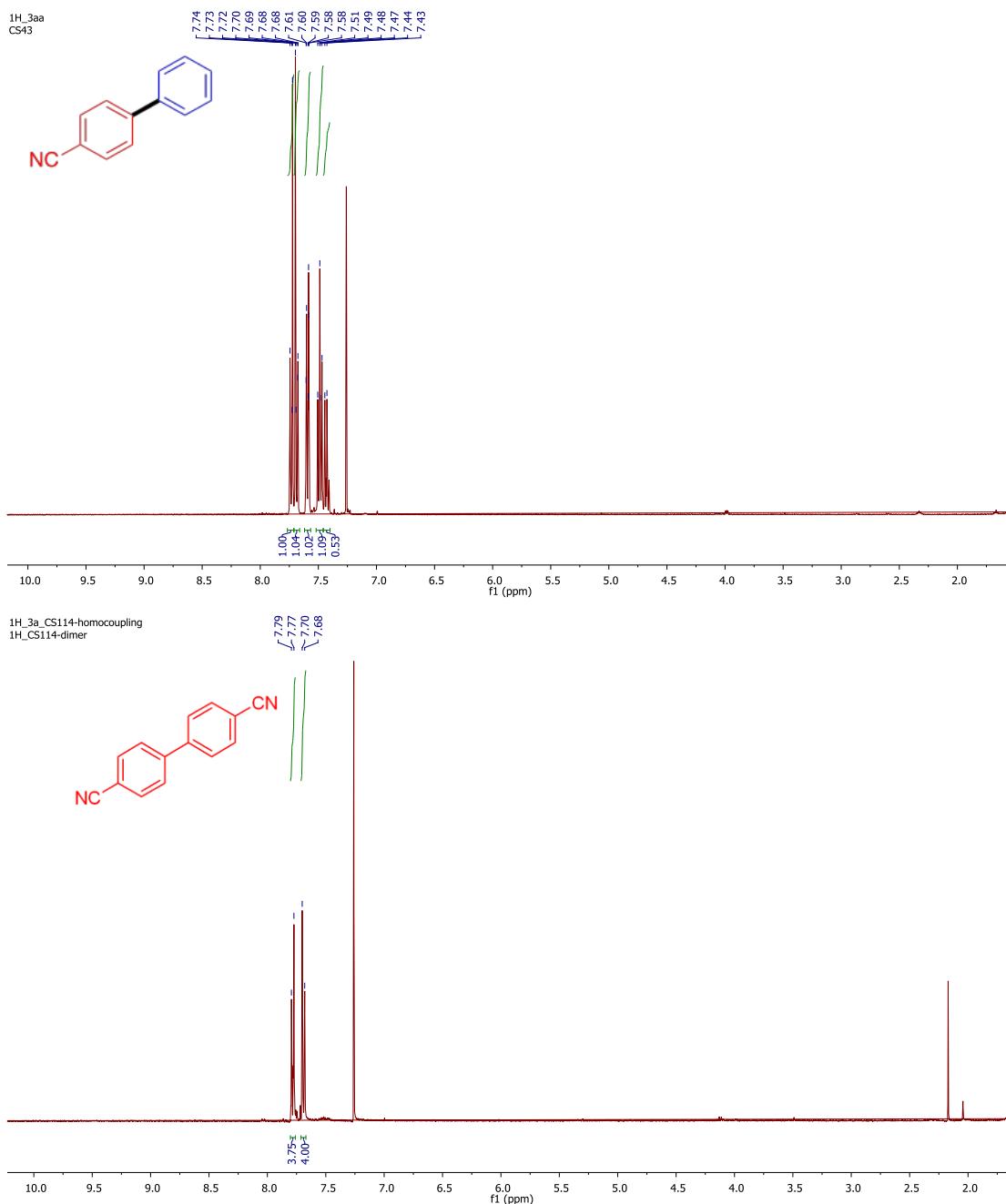
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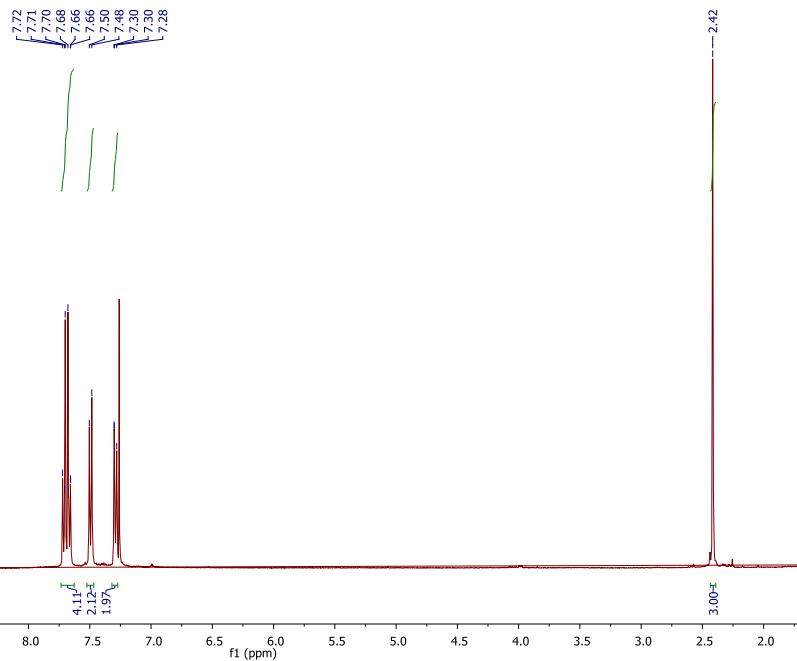
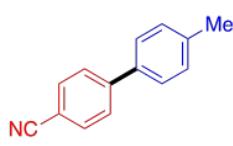
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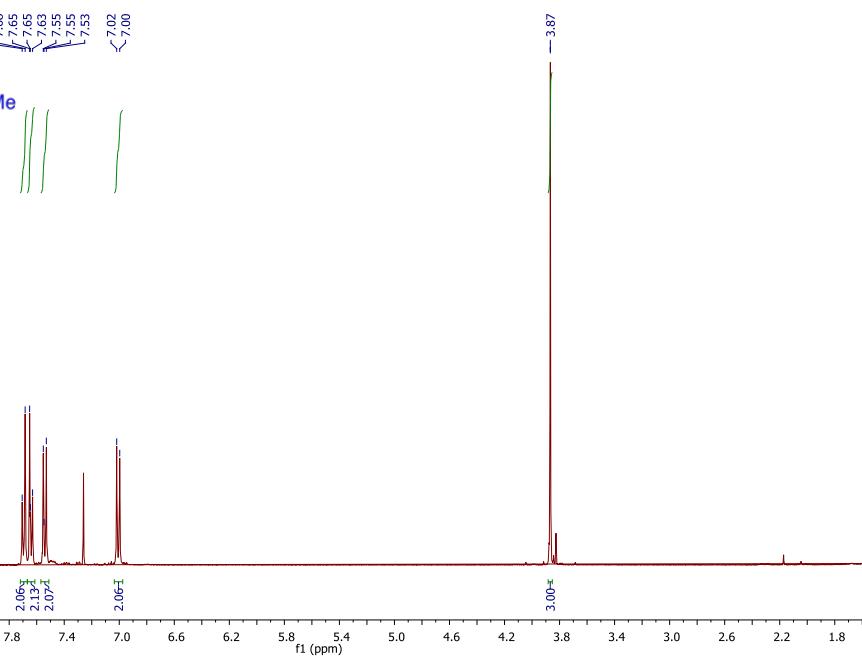
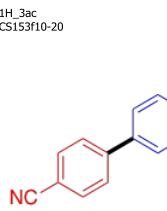
¹H NMR spectra of compounds 3.

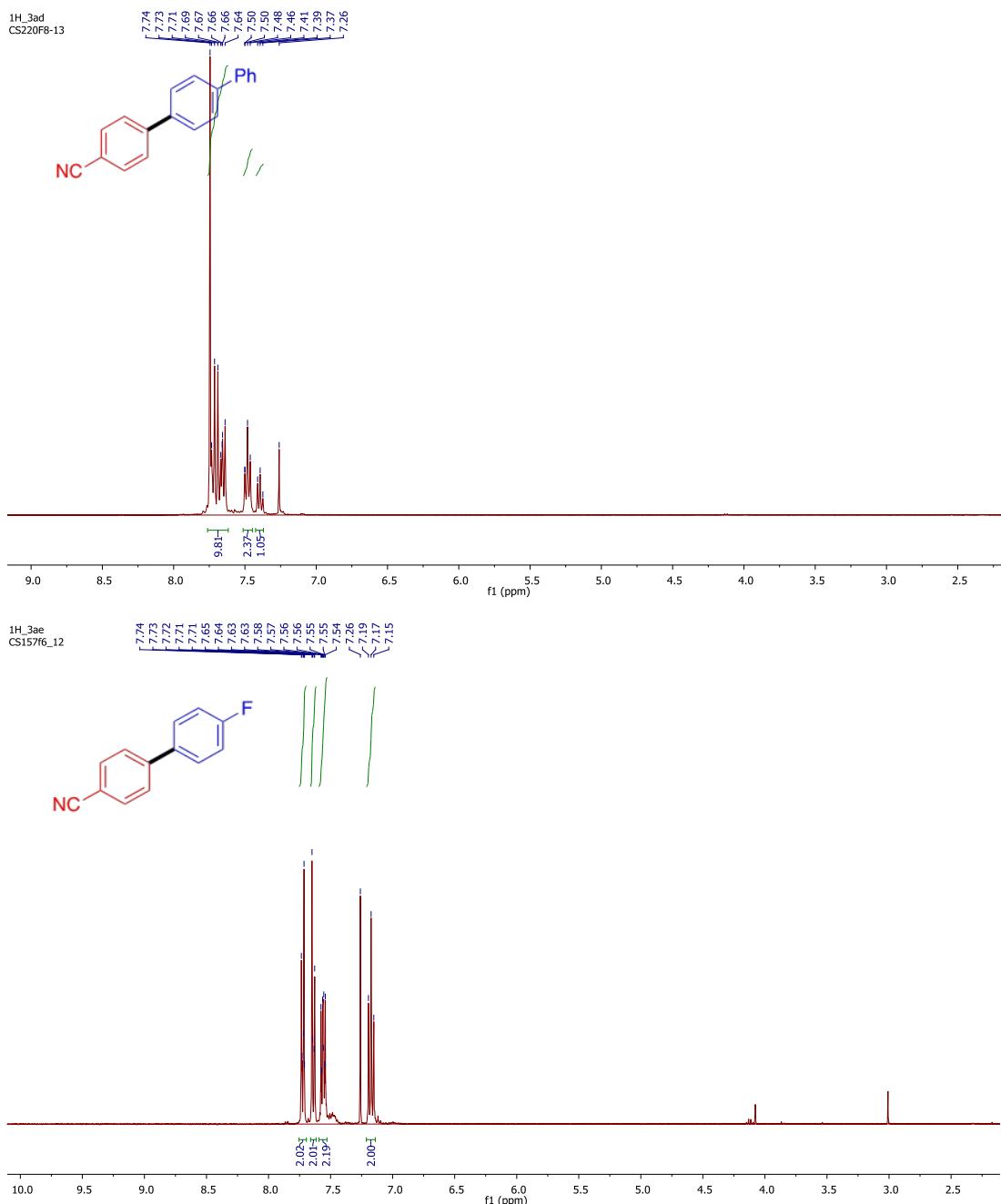


¹H_3ab
CS57new

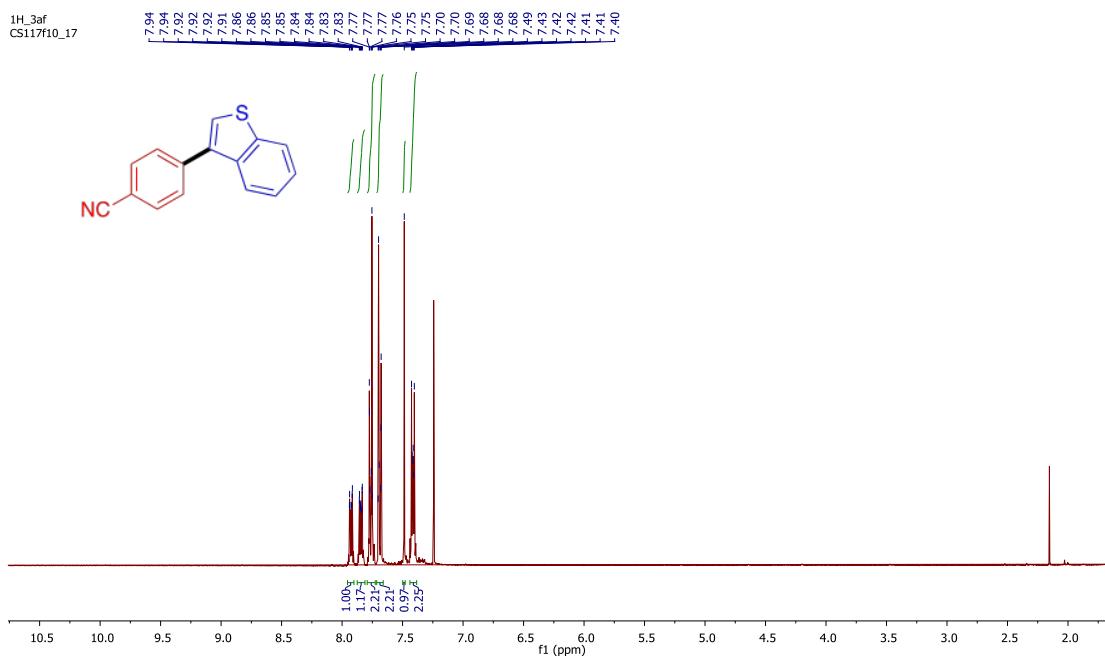


¹H_3ac
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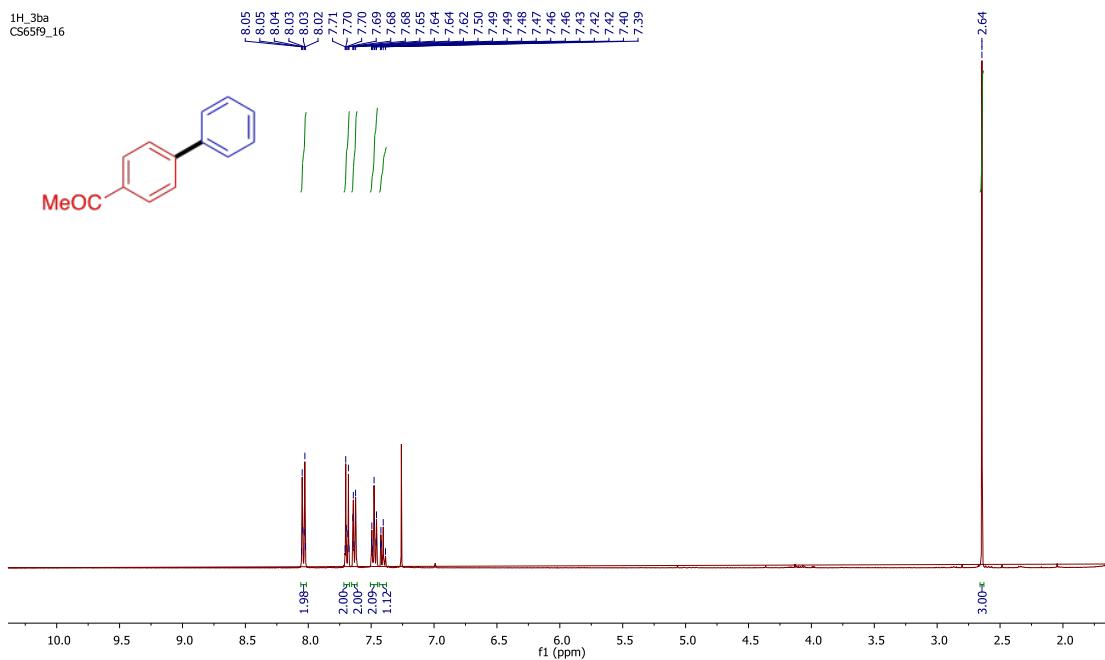




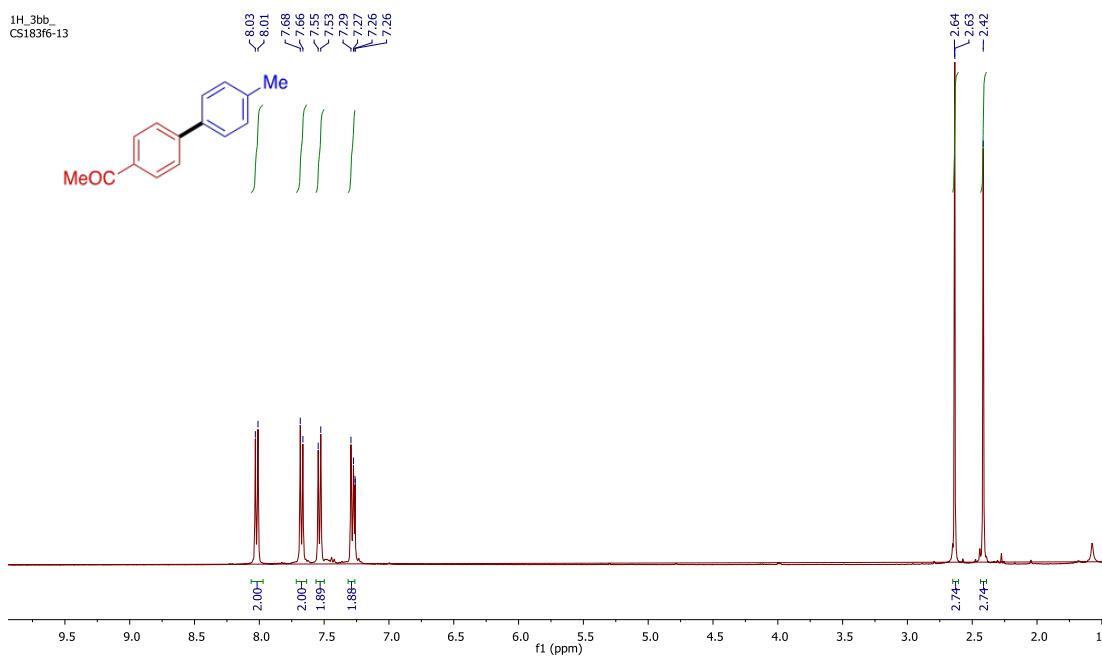
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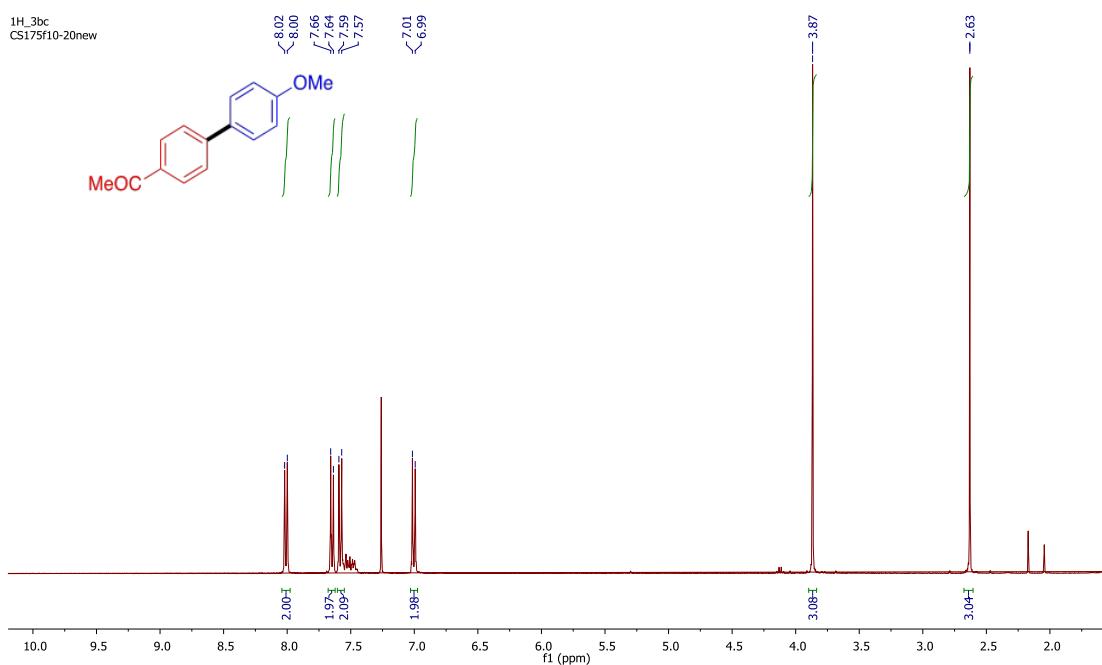
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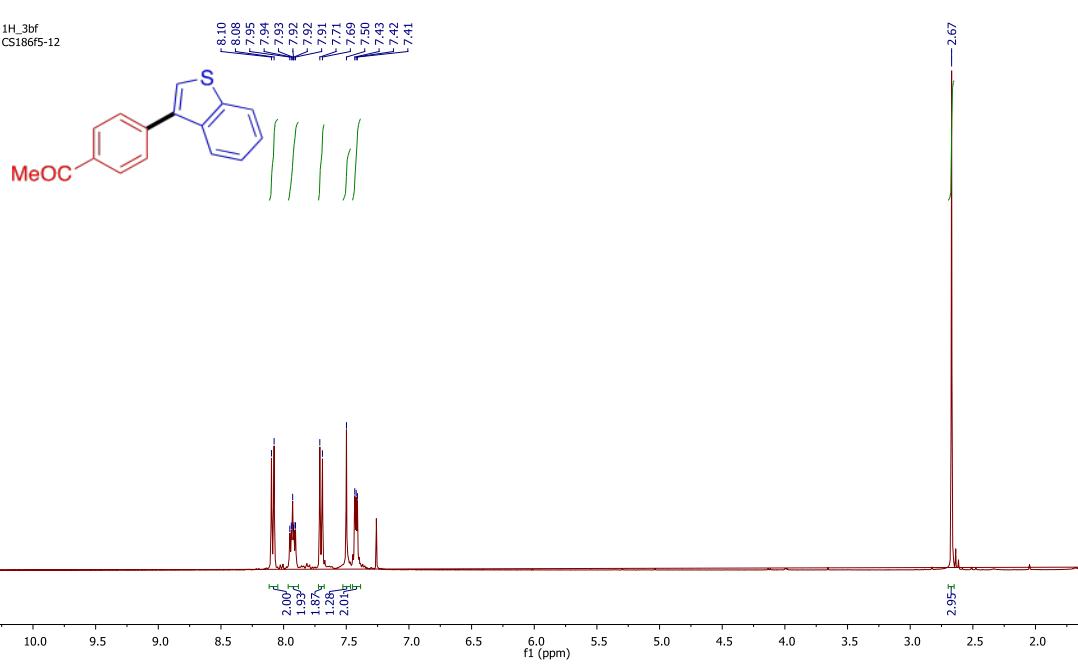
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CS183f6-13



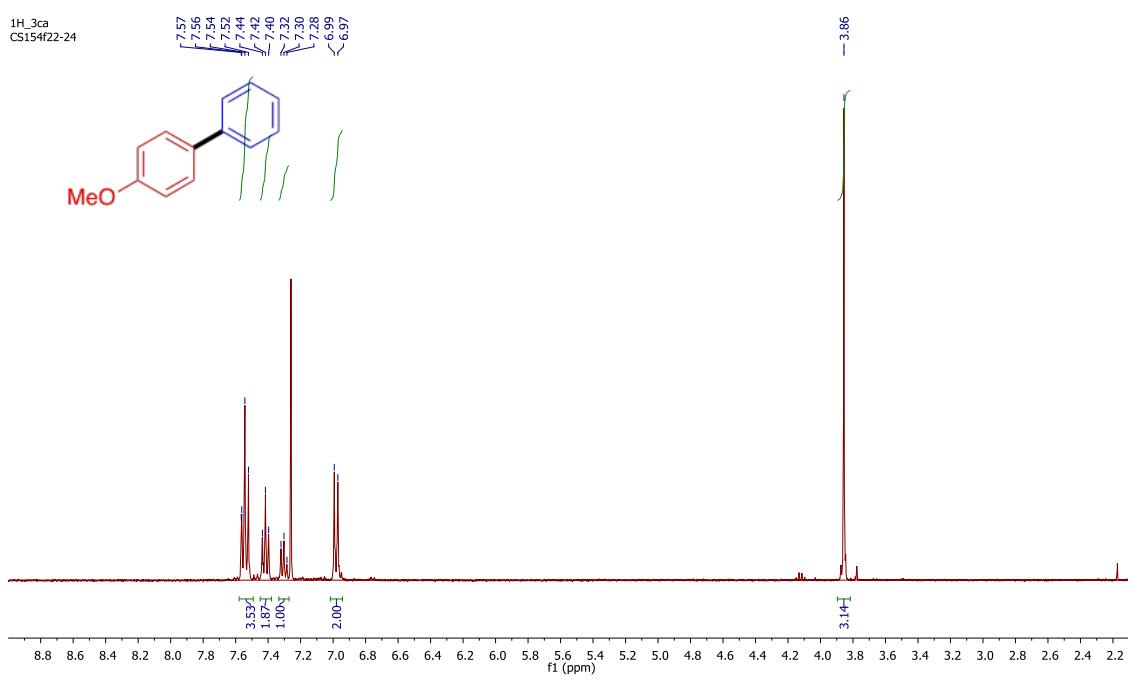
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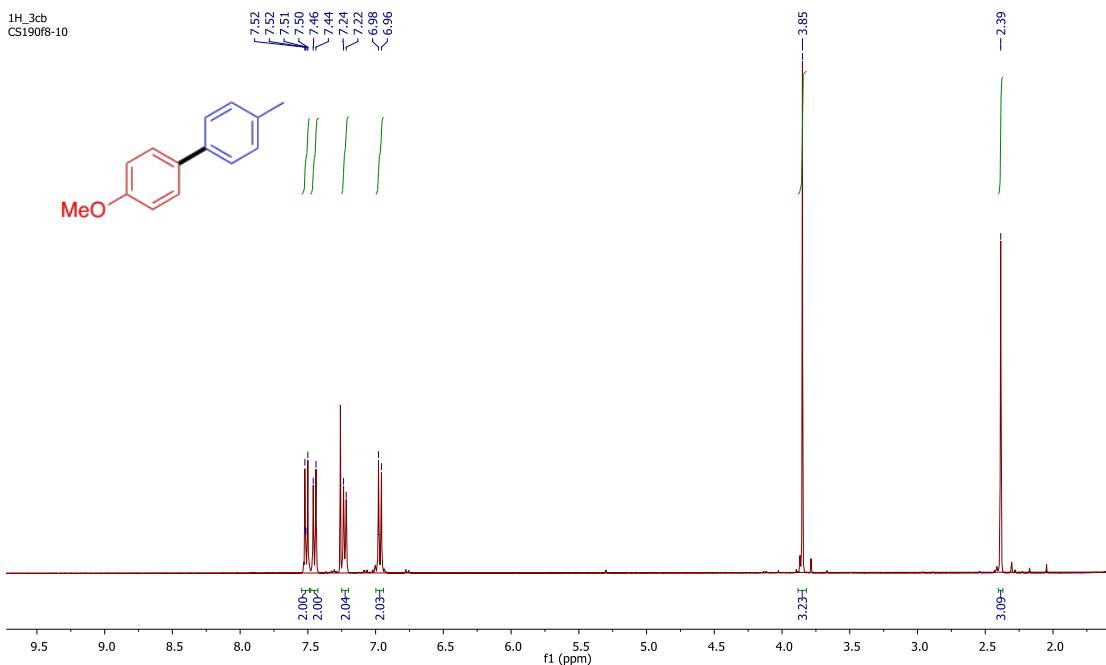
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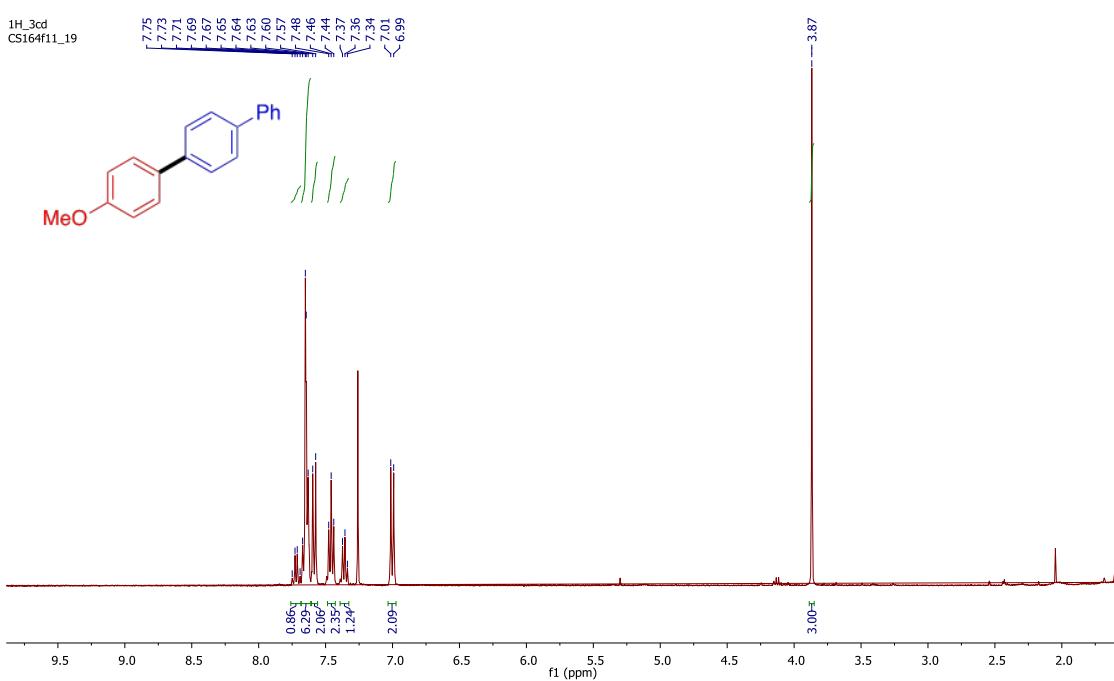
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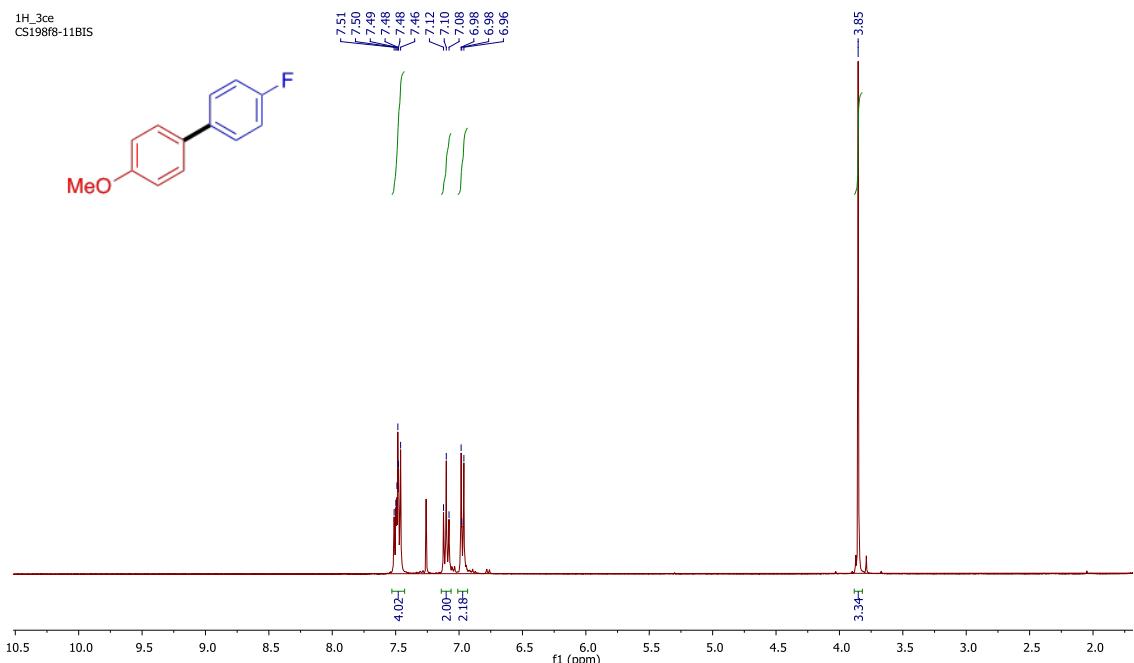
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CS190f8-10



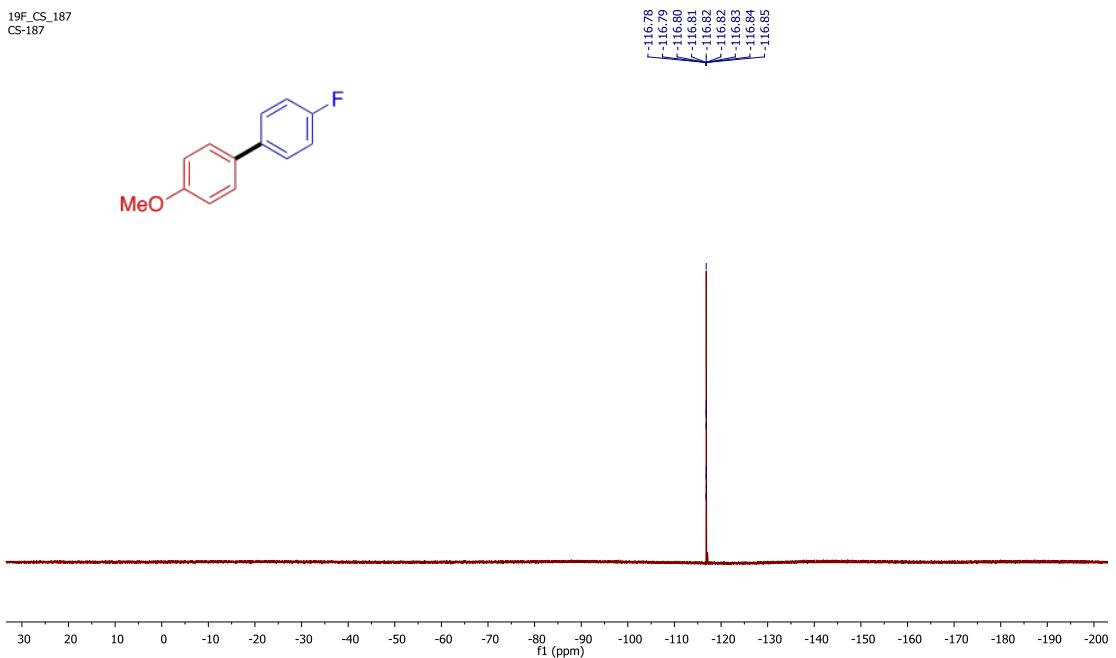
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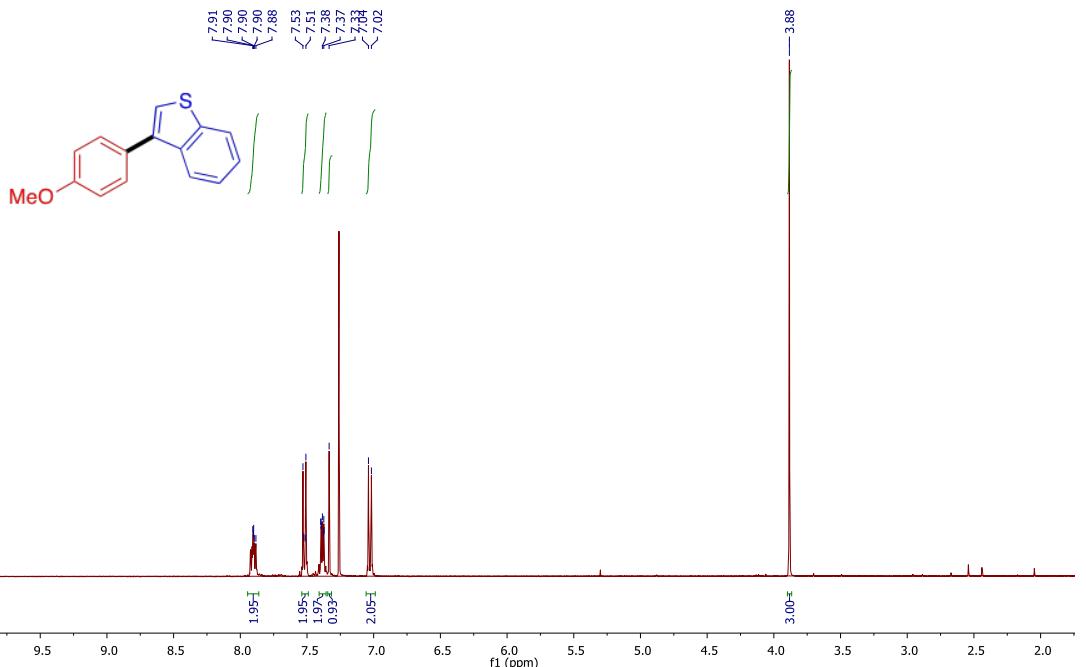
¹H_3ce
CS198f8-11BIS



¹⁹F_CS_187
CS-187



¹H_3cf
CS183f5



¹H_3dc
CS163f8_12

